位能下薛丁格方程式的解

定態 Stationary State

能量的本徵函數

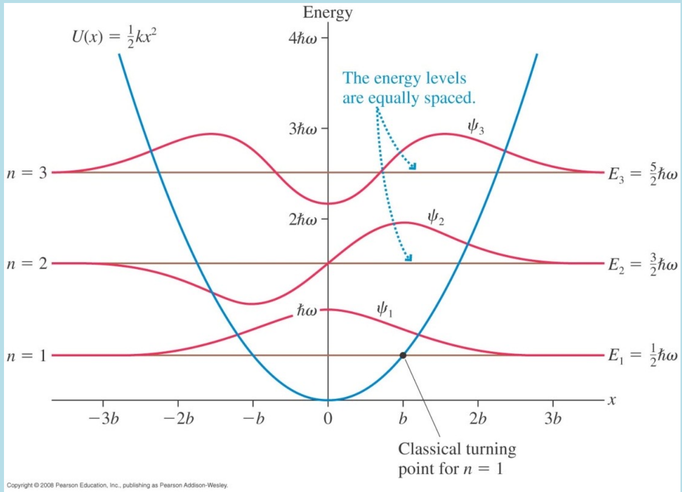
$$H = \frac{p^2}{2m} + V(x)$$

古典

$$\hat{H} \equiv \frac{\hat{p}^2}{2m} + V(\hat{x}) = \frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}\right) + V(x)$$

量子

漢米爾或稱能量算子就定義為動量算子的平方加上位能算子。



薛丁格方程式就可以寫為：

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + V(x)\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

$$\hat{H}\Psi(x,t) = i\hbar\frac{\partial\Psi(x,t)}{\partial t}$$

這就是量子力學完整的薛丁格方程式。

自由空間薛丁格方程式最普遍的求解方式

注意自由電子波與一般波完全不同：時間演化部分與空間部分可以分離。

$$\Psi \sim e^{i(kx-\omega t)} = \left(e^{ikx}\right) \cdot e^{-i\omega t}$$

已知$t = 0$時，$\Psi(x,0)$可以寫成e^{ikx}的疊加，係數$A(k)$為其傅立葉變換：

$$\Psi(x,0) = \int_{-\infty}^{\infty} A(k) \cdot e^{ikx} \cdot dk$$

我們已經確定e^{ikx}的時間演化為$e^{-i\omega(k)t}$。

$$\omega = \frac{\hbar}{2m} k^2$$

因此$\Psi(x,0)$隨時間的演化，也就是個別e^{ikx}演化後的疊加：

$$\Psi(x,t) = \int_{-\infty}^{\infty} A(k) \cdot e^{ikx} e^{-i\omega(k)t} \cdot dk$$

自由電子薛丁格方程式的解就是自由電子波函數的疊加！

如果位能薛丁格方程式也有一系列類似自由電子波這樣的解：

這些解的時間演化部分$\phi(t)$與空間部分$\psi(x)$可以分離separable：

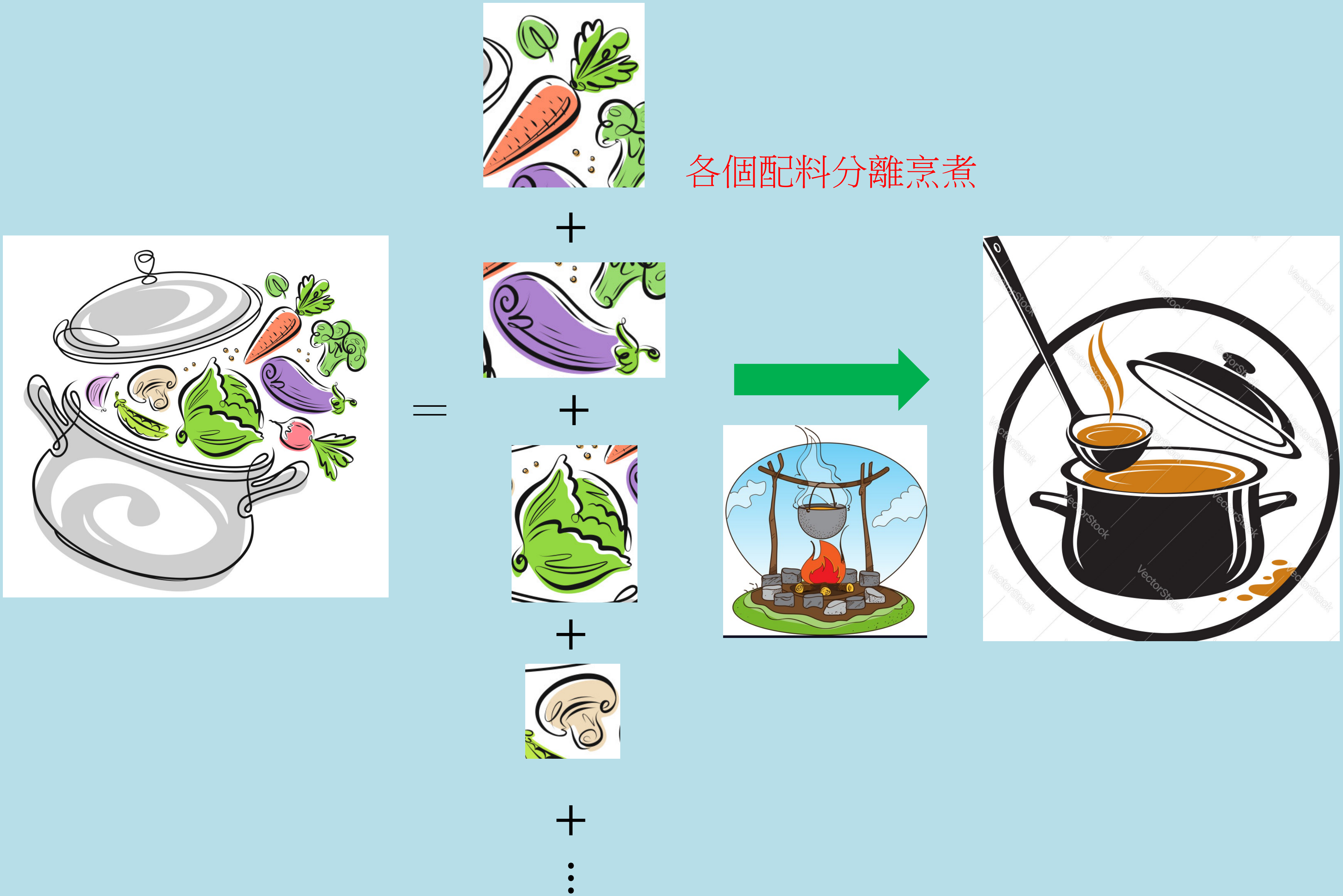
$$\psi_n(x) \cdot \phi_n(t)$$

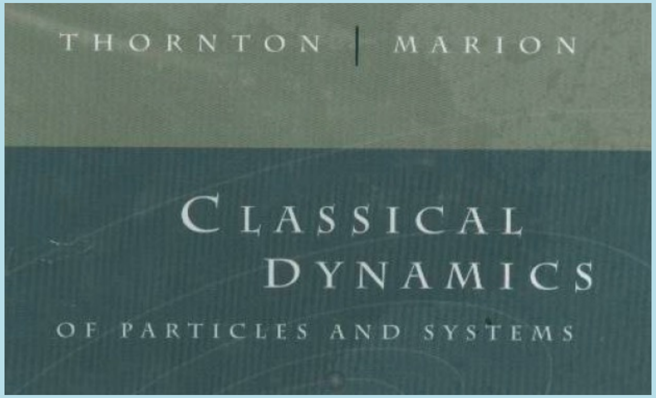
如果$\Psi(x,0)$也可以寫成這一系列的$\psi_n(x)$的疊加，

那就讓個別的$\psi_n(x)$分別依其對應的$\phi_n(t)$演化後，再疊加回來即可：

$$\Psi(x,t) = \sum_{n=1}^{\infty} A_n \psi_n(x) \cdot \phi_n(t)$$

這樣時間部分與空間部分可以分離的解，稱為定態Stationary State 。


各個配料分離烹煮



可以分離separable的解

We now wish to show that Equation 13.65 results naturally from a powerful method that can often be used to obtain solutions to partial differential equations—the method of **separation of variables.** First, we express the solution as

$$\Psi(x, t) \equiv \psi(x) \cdot \chi(t) \tag{13.67}$$

that is, we assume that the variables are *separable* and therefore that the complete wave function can be expressed as the product of two functions, one of which is a spatial function only, and one of which is a temporal function only. It is not guaranteed that we will always find such functions, but many of the partial differential equations encountered in physical problems are separable in at least one coordinate system; some (such as those involving the Laplacian operator) are separable in many coordinate systems. In short, the justification of the method of separation of variables, as is the case with many assumptions in physics, is in its success in producing mathematically acceptable solutions to a problem that eventually are found to properly describe the physical situation, i.e., are "experimentally verifiable."

Solving Wave Equation: $\frac{\partial^2 u}{\partial x^2} = \frac{1}{c^2}\frac{\partial^2 u}{\partial t^2}$,

8.2 THE METHOD OF SEPARATION OF VARIABLES

Since the additional conditions imposed on $u(x, t)$ in our string problem fall into two groups, (a) those involving x (boundary conditions) and (b) those involving t (initial conditions), it may be reasonable to seek solutions of the PDE in the form

$$u(x, t) = X(x)T(t),$$

where X is a function of x only and T is a function of t only. If $X(x)$ is chosen to satisfy the conditions

$$X(0) = 0, \qquad X(L) = 0,$$

then the function $u(x, t)$ will satisfy the same conditions. Then $T(t)$ may, perhaps, be chosen to satisfy the initial conditions.

We now require that $u(x, t)$ satisfy the PDE. We have

$$\frac{\partial^2 u(x,t)}{\partial x^2} = \frac{d^2 X(x)}{dx^2}T(t), \qquad \frac{\partial^2 u(x,t)}{\partial t^2} = X(x)\frac{d^2 T(t)}{dt^2}.$$

Therefore

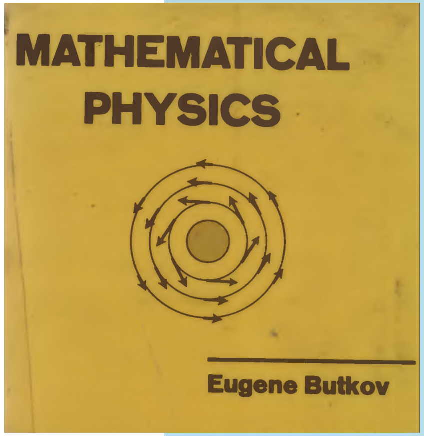
$$\frac{d^2 X}{dx^2}T = \frac{1}{c^2}X\frac{d^2 T}{dt^2}.$$

Dividing both sides by $X(x)T(t)$, we obtain

$$\frac{1}{X}\frac{d^2 X}{dx^2} = \frac{1}{c^2}\frac{1}{T}\frac{d^2 T}{dt^2}.$$

The left-hand side of this equation depends on x alone; the right-hand side depends on t alone. If this equality is to hold for all x and t, it is evident that either side must be a constant (same for both sides):

$$\frac{1}{X}\frac{d^2 X}{dx^2} = \lambda, \qquad \frac{1}{c^2}\frac{1}{T}\frac{d^2 T}{dt^2} = \lambda.$$



定態波函數，時間部分與空間部分可以分離：

$$\Psi(x,t) = \psi(x) \cdot \phi(t)$$

代入薛丁格方程式：

$$-\frac{\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial x^2} + V(x)\Psi = i\hbar\frac{\partial \Psi}{\partial t}$$

得到：

$$-\frac{\hbar^2}{2m}\phi(t)\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x)\phi(t) = i\hbar\psi(x)\frac{d\phi(t)}{dt}$$

左右都除以 $\psi(x) \cdot \phi(t)$ ：

$$\frac{1}{\psi(x)}\left[-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x)\right] = i\hbar\frac{1}{\phi(t)}\frac{d\phi(t)}{dt}$$

現在左邊只與x有關，右邊只與t有關，兩者是獨立變數！

這不可能，唯一例外是左右兩式與兩者都無關，是一常數。設為E。

$$\frac{1}{\psi(x)}\left[-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x)\right] = i\hbar\frac{1}{\phi(t)}\frac{d\phi(t)}{dt} \equiv E$$

$$i\hbar\frac{d\phi(t)}{dt} = E\phi(t)$$

➡

$$\phi(t) = e^{-i\frac{E}{\hbar}t}$$

定態波函數，時間部分不只可以被分離，而且可以被完全決定，

時間部分與位能$V(x)$的關係完全濃縮在一個常數E之中！

$$\phi(t) = e^{-i\frac{E}{\hbar}t}$$

$$\Psi(x,t) = \psi_E(x) \cdot e^{-i\frac{E}{\hbar}t} = \psi_E e^{-i\omega t}$$

定態波函數的時間演化就是函數$\psi_E(x)$乘上一個Phase factor：$e^{-i\frac{E}{\hbar}t}$。

如同自由電子波一樣！

$E = \hbar\omega$顯然就是能量。

大膽推測：對這些解， E就是能量的測量結果，

之後我們將正式證明對於定態，能量的測量的確沒有不確定性！ $\Delta E = 0$

可以被分離的波函數，

$$\Psi(x,t)=\psi_E(x)\cdot e^{-i\frac{E}{\hbar}t}=\psi_E e^{-i\omega t}$$

$\psi_E(x)$是時間為零時的瞬間波函數$\Psi(x,0)$，$e^{-i\frac{E}{\hbar}t}$是未來的演化evolution。

量子波函數若可以分離，稱為定態，它所有可測量的量都與時間無關。

機率密度 $P=|\Psi|^2=\left|\psi_E(x)\cdot e^{-i\frac{E}{\hbar}t}\right|^2=|\psi_E(x)|^2\left|e^{-i\frac{E}{\hbar}t}\right|^2=|\psi_E(x)|^2$ 與時間無關。

其他物理測量的期望值也都與時間無關！

$$\langle f(x,p)\rangle=\int_{-\infty}^{\infty}dx\cdot\psi_E^*(x)e^{i\frac{E}{\hbar}t}f\left(x,-i\hbar\frac{\partial}{\partial x}\right)\psi_E(x)e^{-i\frac{E}{\hbar}t}$$

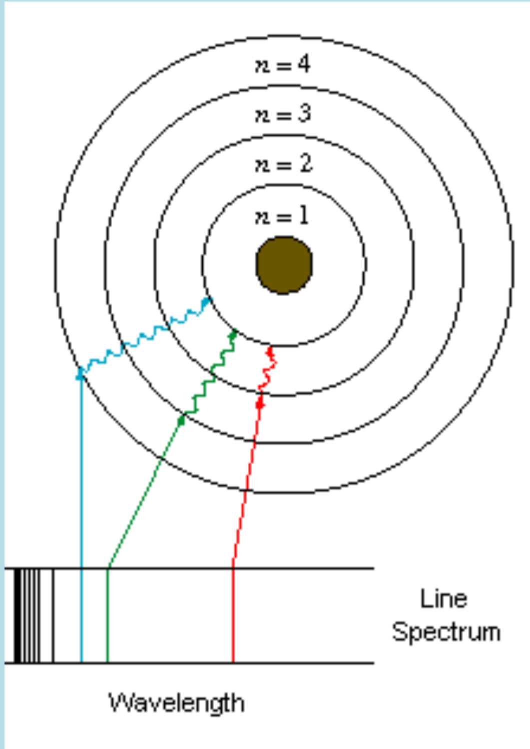
$$=\int_{-\infty}^{\infty}dx\cdot\psi_E^*(x)f\left(x,-i\hbar\frac{\partial}{\partial x}\right)\psi_E(x)$$

自由電子波是定態 Stationary State

在定態中，所有對電子的測量結果，都與時間無關！

牛頓力學中，唯一的定態，就是靜止狀態！

但量子力學中，卻有許多定態。



波爾的原子模型中的電子穩定軌道即是定態！

Stationary 駐立 Stable 穩定。

但定態並不一定永遠穩定，電磁場會使原本的定態成為激發態，成為不穩定。

6.1 Stationary States

Stationary states are a class of simple and useful solutions of the Schrödinger equation. They give us intuition and help us build up general solutions of this equation. Stationary states have time dependence, but this dependence is so simple that in such states observables are in fact time independent. For the case of a particle moving in a potential, stationary states exist if the potential is time independent.

$$\Psi(x,t) = \psi_E(x) \cdot e^{-i\frac{E}{\hbar}t}$$

時間只改變了$\psi_E(x)$在複數平面的相角 Phase。

物理測量只與$\psi_E(x)$的絕對值有關，獨立的phase變化沒有物理結果。

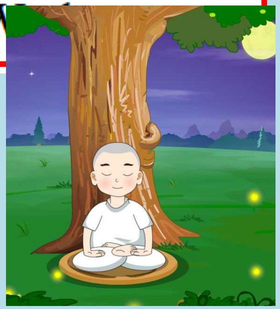
因此可以說定態的電子一直是處於同一個狀態！就是$\psi_E(x)$所決定的電子狀態。

空間部分函數$\psi_E(x)$沒有隨時間變！只是換了不同版本！

While a stationary state wave function $\Psi(x, t) = e^{-iEt/\hbar}\psi(x)$ depends on time, it is physically time independent. This is, in fact, the content of observation (1) above; no expectation value shows time dependence. We can see this time independence more conceptually as follows. Consider the stationary state at time t and at time $t + t_0$, with t_0 some arbitrary constant time. We see that

$$\Psi(x, t + t_0) = e^{-iE(t+t_0)/\hbar}\psi(x) = e^{-iEt_0/\hbar}\,\Psi(x,t). \qquad (6.1.22)$$

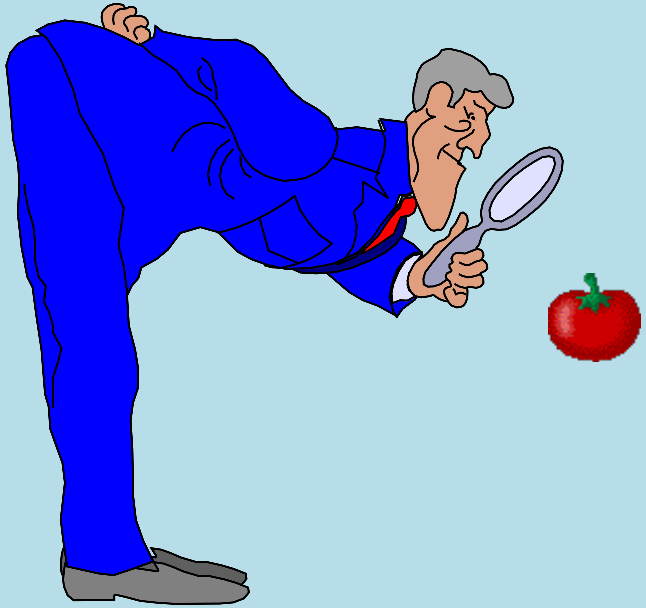
Since the stationary-state wave functions at t and at $t + t_0$ differ by an overall *constant* phase, they are physically equivalent, they are the *same* state. The phase is a constant because it has no t or x dependence. W

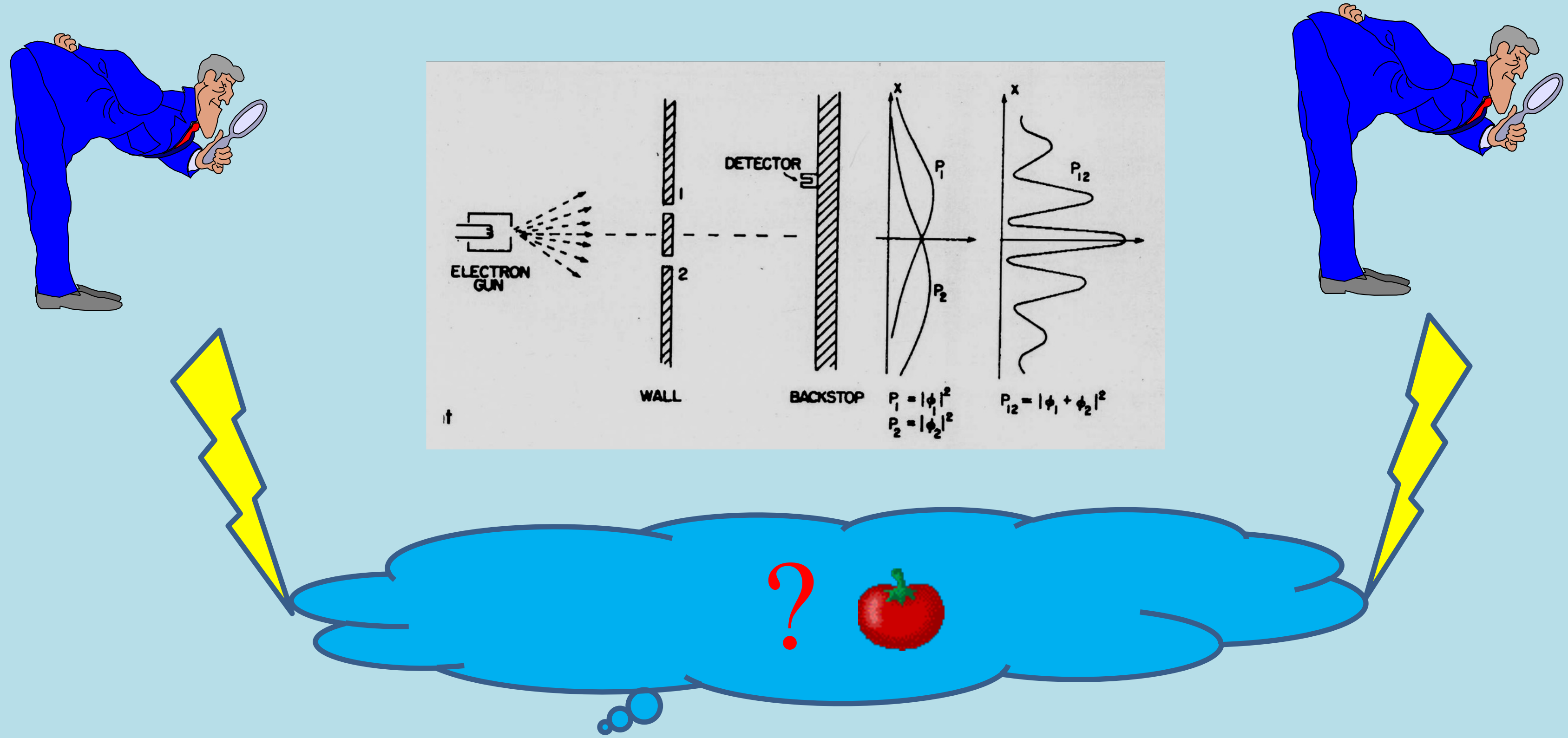


因此起始條件若在定態，此電子就會一直留在此定態！

無人打擾時，電子會獨立逗留的狀態，就是定態。

觀察的巨觀儀器與被觀察的微觀系統，在尺度上有巨大差異！
巨觀的儀器無法長期地追蹤微觀的系統。

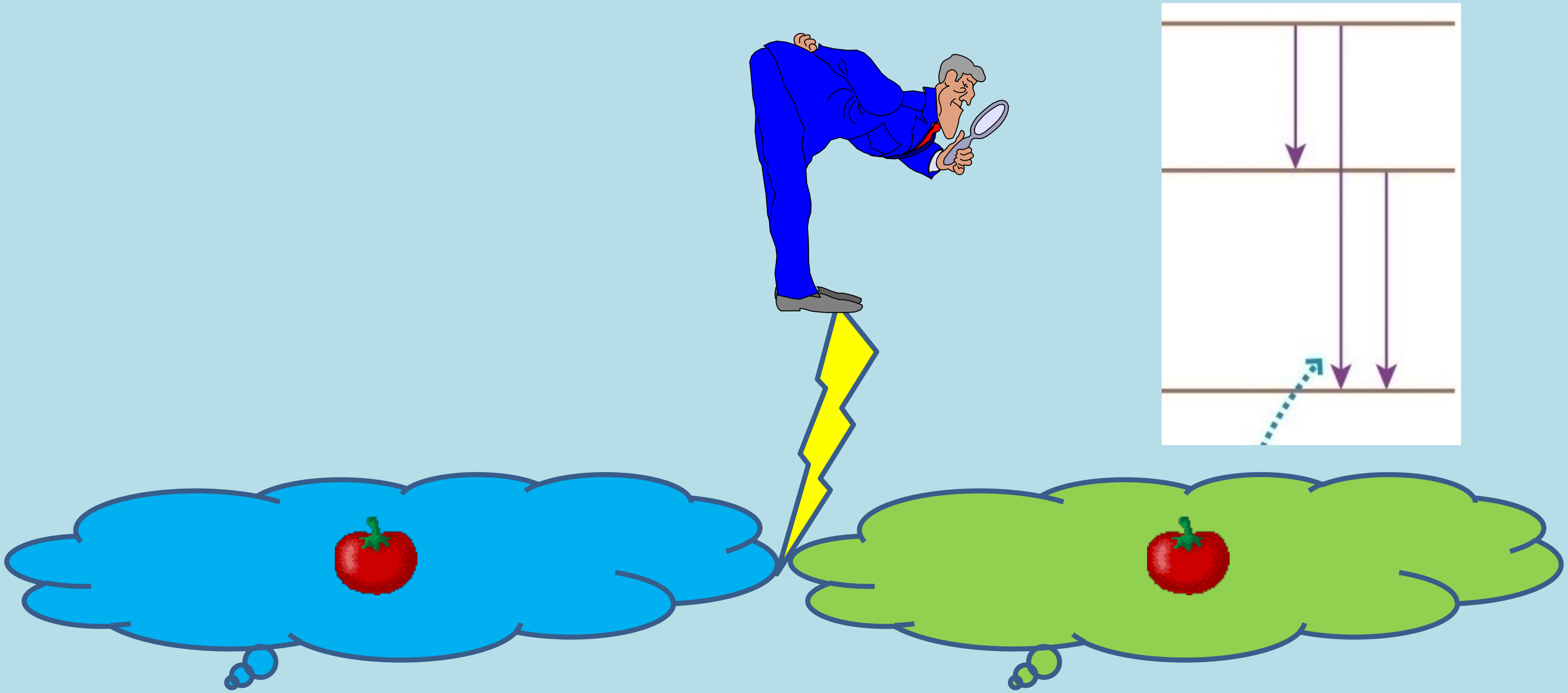




巨觀的儀器無法長期地追蹤微觀的系統。

只能於前後作設定及測量。

在兩者之間微觀系統就獨立地維持定態。



或者之前獨立演化的微觀系統。

在巨觀儀器干擾後，躍遷至另一狀態。

例如：電磁場可以引發一顆光子的放射吸收，

會使原本穩定的定態，可以躍遷到其他的定態。

在躍遷之前之後，獨立的微觀系統維持處於一定態！

時間部分已解出，現在我們來寫定態解空間位置部分$\psi(x)$滿足的方程式：

定態解的特點是：時間部分與空間部分分離。

$$\frac{1}{\psi(x)}\left[-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}+V(x)\psi(x)\right]=i\hbar\frac{1}{\phi(t)}\frac{d\phi(t)}{dt}\equiv E$$

位置函數$\psi(x)$對應特定的E，因此將E寫在足標：$\psi_E(x)$：

$\psi_E(x)$滿足此常微分方程式：

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_E(x)}{dx^2}+V(x)\cdot\psi_E(x)=E\cdot\psi_E(x)$$

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)\right]\psi_E(x)=E\cdot\psi_E(x)$$

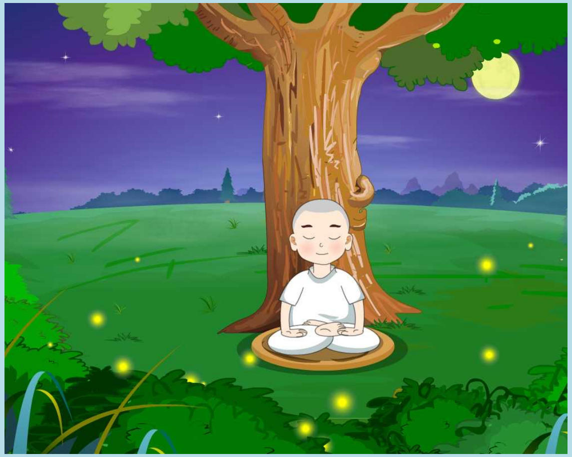
Time-Independent Schrodinger Equation

與時間無關之薛丁格方程式。

與時間無關之薛丁格方程式。

定態波函數的空間部分所滿足的方程式：

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_E(x)}{dx^2} + V(x)\cdot\psi_E(x) = E\cdot\psi_E(x)$$

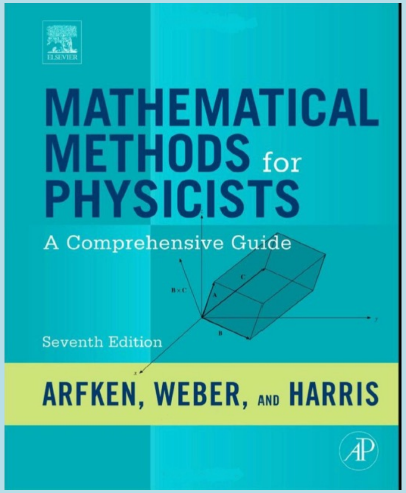


解出位置函數$\psi_E(x)$， 整個定態波函數$\Psi(x,t)$就都知道了！

$$\Psi(x,t) = \psi_E(x)e^{-i\frac{E}{\hbar}t}$$

方程式中不再有i，解可以是實數。

這是一個典型古典物理的Sturm-Liouville Theory!



$$-\frac{\hbar^2}{2m}\frac{d^2\psi_E(x)}{dx^2}+V(x)\cdot\psi_E(x)=E\cdot\psi_E(x)$$

CHAPTER 8

STURM-LIOUVILLE THEORY

Characterization of the general features of eigenproblems arising from second-order differential equations is known as **Sturm-Liouville theory**. It therefore deals with eigenvalue problems of the form

$$\mathcal{L}\psi(x)=\lambda\psi(x), \tag{8.7}$$

where $\mathcal{L}$ is a linear second-order differential operator, of the general form

$$\mathcal{L}(x)=p_0(x)\frac{d^2}{dx^2}+p_1(x)\frac{d}{dx}+p_2(x). \tag{8.8}$$

The key matter at issue here is to identify the conditions under which $\mathcal{L}$ is a Hermitian operator.

在很多情況下，這個方程式只對某一些能量E，可以得到解。

這些能量E，稱為本徵值 Eigenvalues，

對應的解$\psi_E(x)$稱為漢米爾頓量的本徵函數 Eigenfunction。

本徵值E，若是離散分布，能量就是量子化的！

Quantization as an Eigenvalue Problem 1926

能量的量子化作為（不過就是）一個本徵值問題

3. ***Quantisierung als Eigenwertproblem;***
von E. Schrödinger.

(Erste Mitteilung.)

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§ 1. In dieser Mitteilung möchte ich zunächst an dem einfachsten Fall des (nichtrelativistischen und ungestörten) Wasserstoffatoms zeigen, daß die übliche Quantisierungsvorschrift sich durch eine andere Forderung ersetzen läßt, in der kein Wort von „ganzen Zahlen" mehr vorkommt. Vielmehr ergibt sich die Ganzzahligkeit auf dieselbe natürliche Art, wie etwa die Ganzzahligkeit der *Knotenzahl* einer schwingenden Saite. Die neue Auffassung ist verallgemeinerungsfähig und rührt, wie ich glaube, sehr tief an das wahre Wesen der Quantenvorschriften.

Die übliche Form der letzteren knüpft an die Hamiltonsche partielle Differentialgleichung an:

(1) $$H\left(q, \frac{\partial S}{\partial q}\right) = E\,.$$

Es wird von dieser Gleichung eine Lösung gesucht, welche sich darstellt als *Summe* von Funktionen je einer einzigen der unabhängigen Variablen q.

Wir führen nun für S eine neue unbekannte ψ ein derart, daß ψ als ein *Produkt* von eingriffigen Funktionen der einzelnen Koordinaten erscheinen würde. D. h. wir setzen

(2) $$S = K \lg \psi\,.$$

Die Konstante K muß aus dimensionellen Gründen eingeführt werden, sie hat die Dimension einer *Wirkung*. Damit erhält man

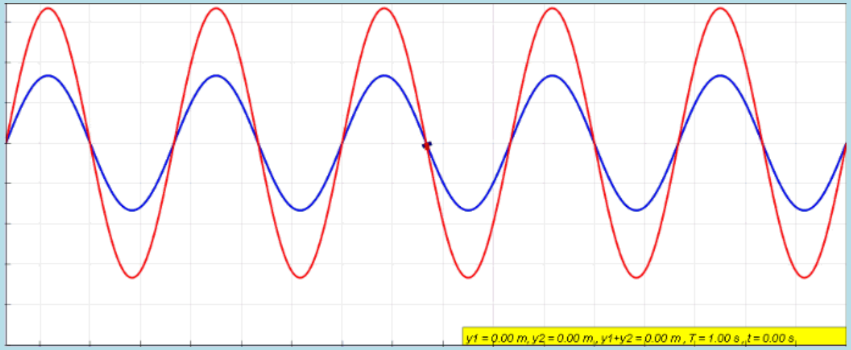
(1′) $$H\left(q, \frac{K}{\psi}\frac{\partial \psi}{\partial q}\right) = E\,.$$

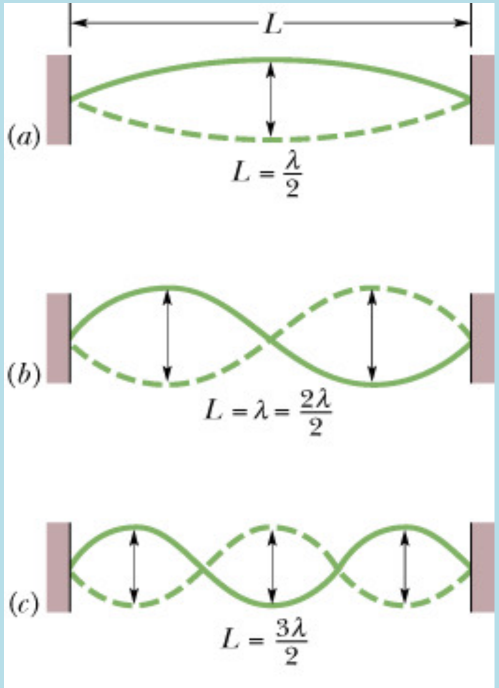
Wir suchen nun *nicht* eine Lösung der Gleichung (1′), sondern

以上定態的概念其實是老朋友了，繩波理論中，我們找到穩定的駐波態就是。

$$y = \left(2y_m \cdot \sin\frac{n\pi}{a}x\right) \cdot \cos\omega t$$

整條弦都被同一個時間函數所控制，整條弦一起振盪，所以波函數是可分離的。

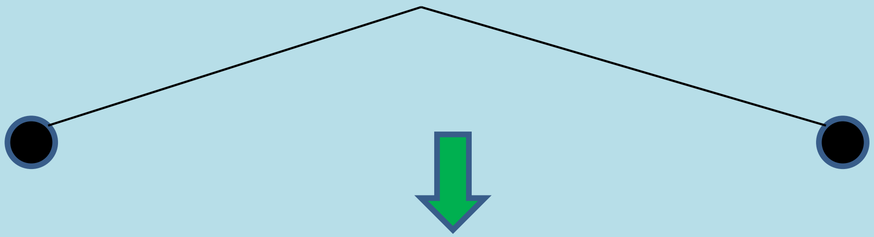




兩端固定的弦的任一起始條件可以用駐波模式的疊加來得到

$$y(x,0)=\sum_n a_n \sin\frac{n\pi}{a}x$$

第 n 態的振幅或分量

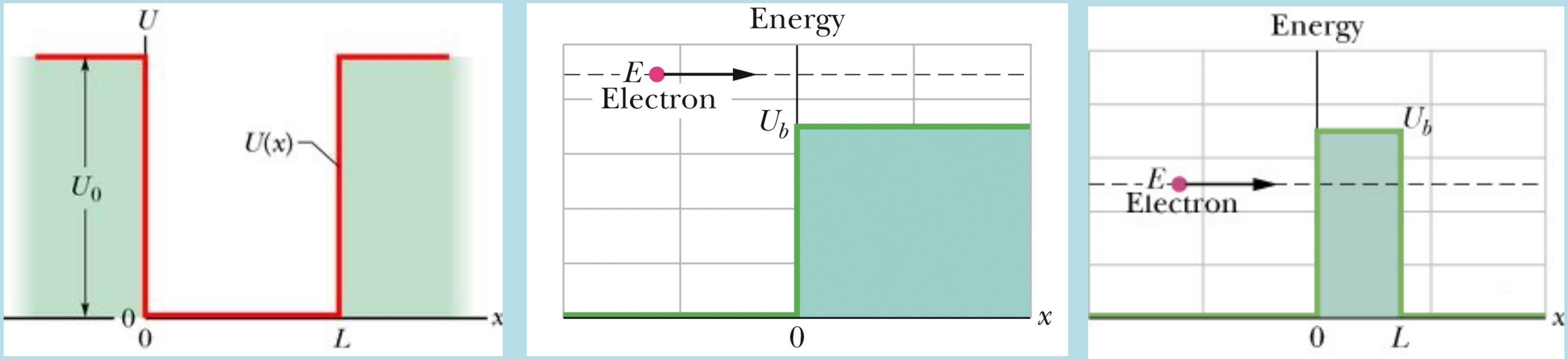


$$y(x,t)=\sum_n a_n \sin\frac{n\pi}{a}x\cos\omega_n t$$

$$y(x,t)\sim \sin\frac{\pi}{a}x\cos\omega_1 t-\frac{1}{9}\sin\frac{3\pi}{a}x\cos\omega_3 t+\cdots$$

可證：兩端固定的弦的運動就是以各個駐波態各自演化後再疊加的波函數運動！

一維階梯狀位能下的定態



一維位能下的定態，如古典物理，大致可以分為束縛態與非束縛態！

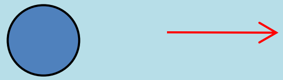
在束縛的情況中，定態的能量通常將出現量子化！

在非束縛的情況中，定態解能組成入射波包，可以描述散射問題！

我們先兩者分別討論一個最簡單的例子。

從非束縛態開始。

首先是大家已經很熟悉的自由電子波，這也是定態！



當電子受力為零時，位能V是一常數， $V(x) = V_0$

不直接設為零，是因為所得結果，將來可以在其他一維階梯狀位能直接引用。

$$\frac{d^2\psi_E}{dx^2} = \frac{2m}{\hbar^2}[V(x) - E]\psi_E = \frac{2m}{\hbar^2}[V_0 - E]\psi_E$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_E}{dx^2} + V(x)\psi_E = E\psi_E$$

假設 $E > V_0$

$$\frac{d^2\psi_E}{dx^2} = \frac{2m}{\hbar^2}[V_0 - E]\psi_E \equiv -k^2\psi_E$$

動能

$$k \equiv \sqrt{\frac{2m}{\hbar^2}(E - V_0)}$$

很容易猜到這就是角波數。

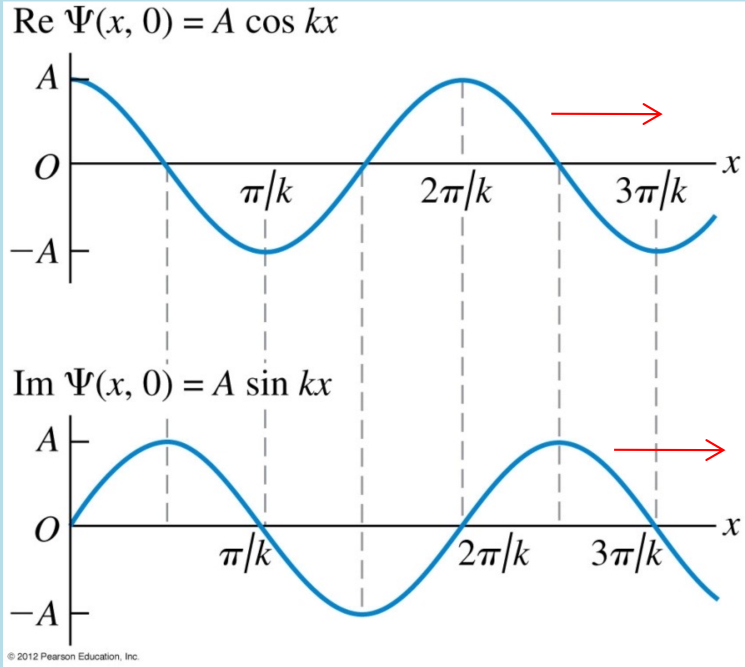
其解很簡單，二次微分後與自己成正比，就是指數函數 $\frac{d^n}{dx^n}e^{ax} = (a)^n \cdot e^{ax}$

$a^2 = -k^2$ $a = \pm ik$ a有兩個解！

$$\psi_E = Ae^{ikx} + Be^{-ikx}$$

這是二次微分方程式，上式有兩個未知係數，因此已經是最普遍的解了

自由空間的電子定態



$$\psi_E = Ae^{ik(E)x} + Be^{-ik(E)x}$$

$$k(E) \equiv \sqrt{\frac{2m}{\hbar^2}(E - V_0)}$$

完整的波函數：

$$\Psi(x,t) = \psi_E(x) \cdot e^{-i\frac{E}{\hbar}t} = Ae^{i\left[\sqrt{\frac{2m}{\hbar^2}(E-V_0)}x-\frac{E}{\hbar}t\right]} + Be^{-i\left[\sqrt{\frac{2m}{\hbar^2}(E-V_0)}x+\frac{E}{\hbar}t\right]}$$

相位分別向$+x$與$-x$方向運動！這當然就是已經解過的平面正弦自由電子波。

當時以角波數k來標記，k決定$\omega(k)$，現在倒過來以能量E來標記，決定$k(E)$。

任意的E數值，只要大於V_0，定態方程式都有解！能量值是連續分布的。

$$\Psi(x,t) = Ae^{i\left[k(E)x - \frac{E}{\hbar}t\right]}$$

$$P = |\Psi|^2 = |A|^2$$

單一角波數k的電子波定態，波長確定，動量確定，機率密度為一常數。

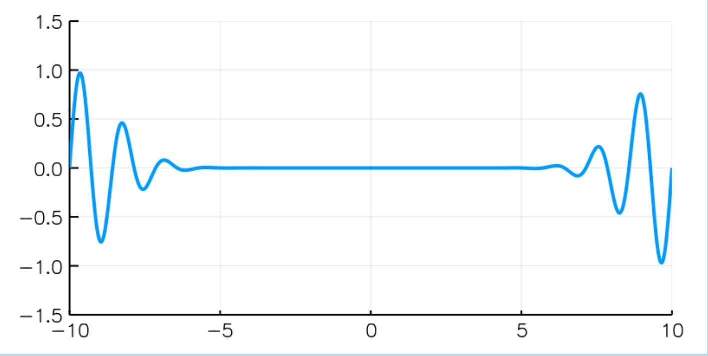
沒有任何位置資訊，

它只是擁有+x方向的動量，但並沒有任何東西是在傳播之中。

畢竟這是定態的電子，它的物理當然完全不隨時間變化。

波包並不是定態，而是能量接近、類似的定態的疊加。

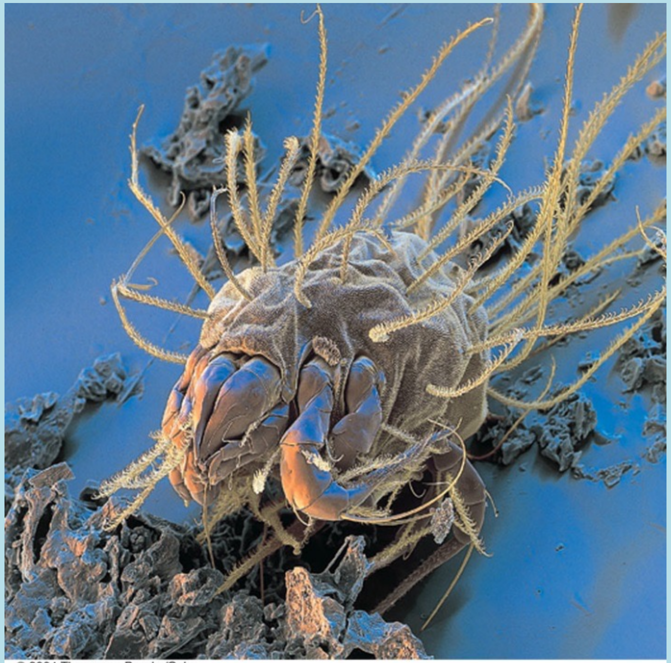
所以中心位置，及位置平均值會移動！



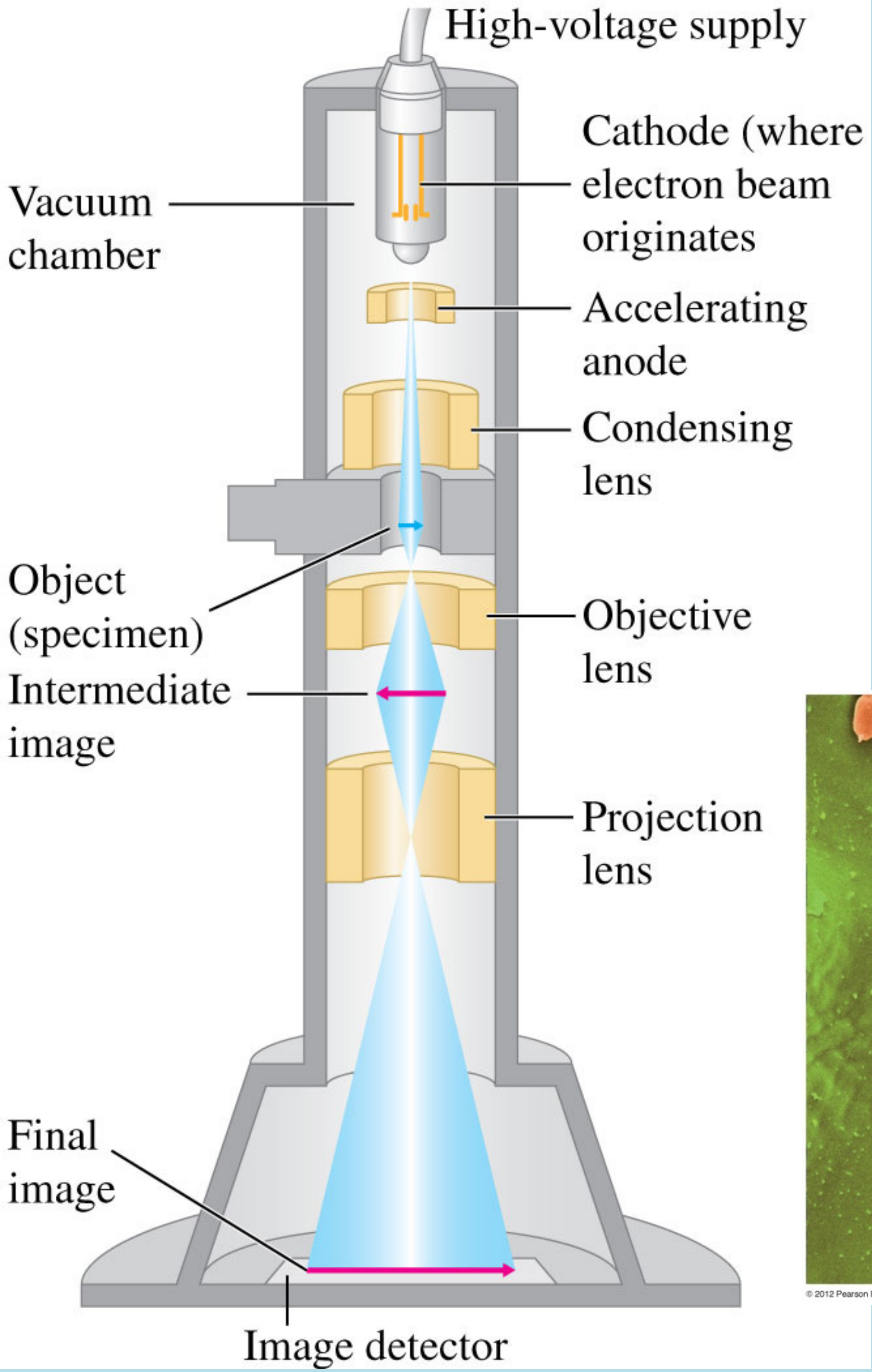
$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}}$$

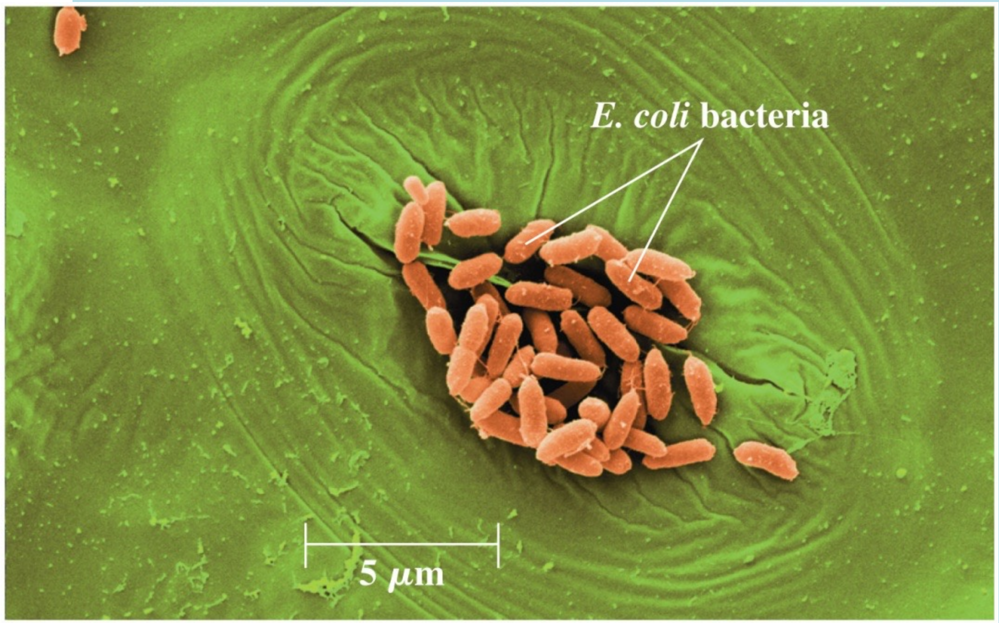
以0.1c光速移動的電子 $\lambda \sim 7.28 \times 10^{-11}\mathrm{m}$

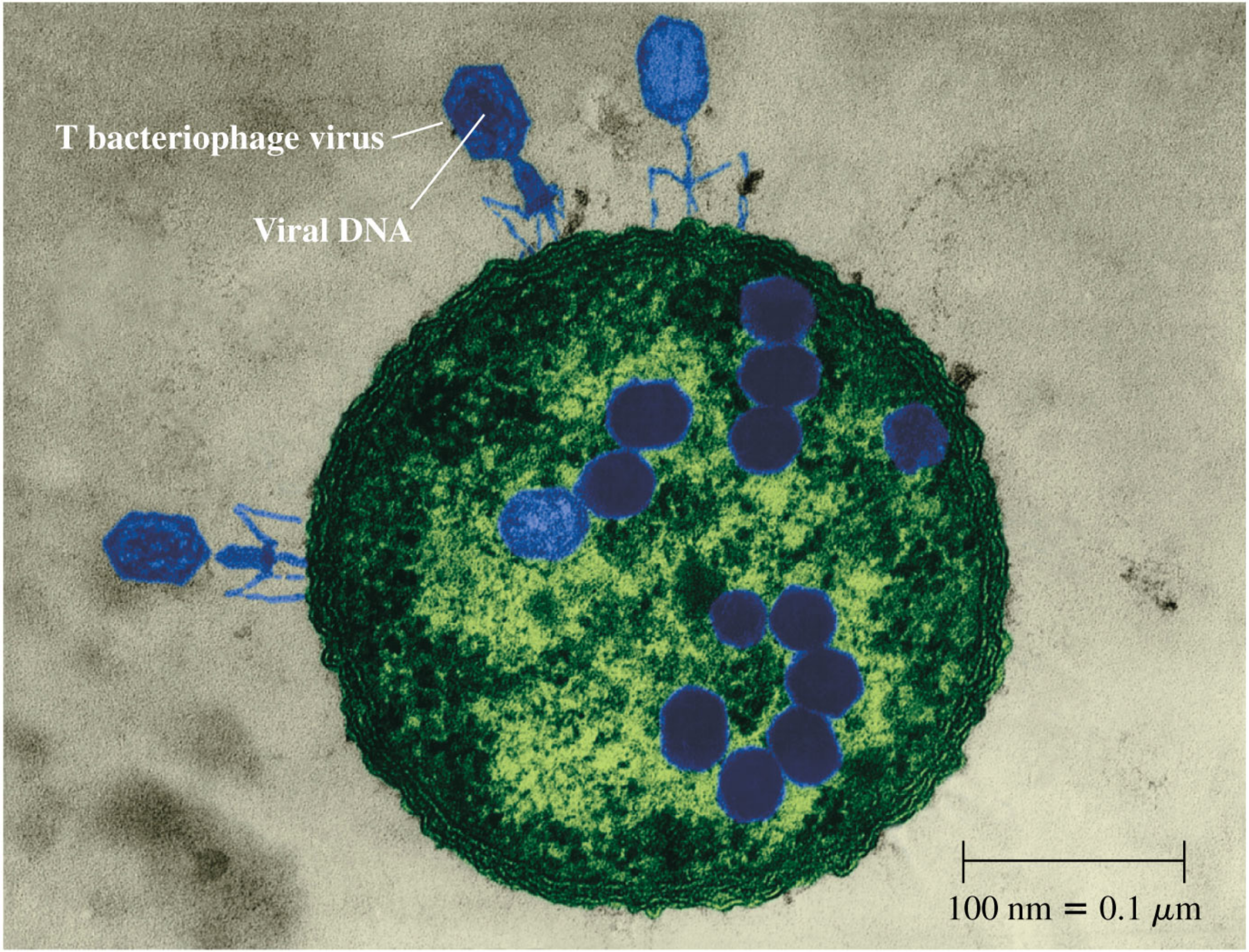
電子波的波長大致是原子尺度，極小，因此在日常生活無法察覺！



極小的波長，使電子波顯微鏡鑑別度極高！


High-voltage supply
Cathode (where electron beam originates
Vacuum chamber
Accelerating anode
Condensing lens
Object (specimen)
Objective lens
Intermediate image
Projection lens
Final image
Image detector

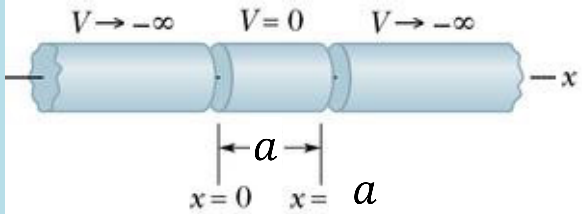

E. coli bacteria
5 μm

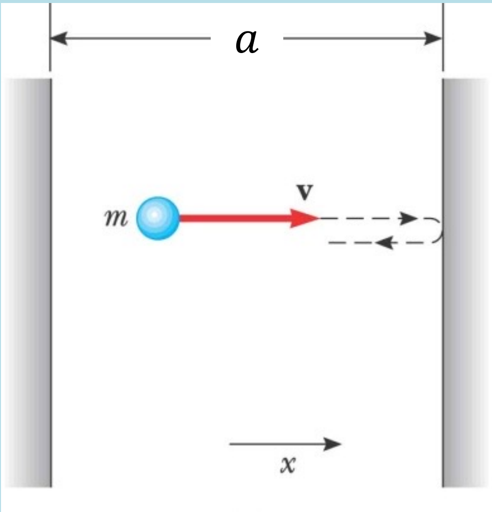

T bacteriophage virus
Viral DNA
100 nm = 0.1 μm

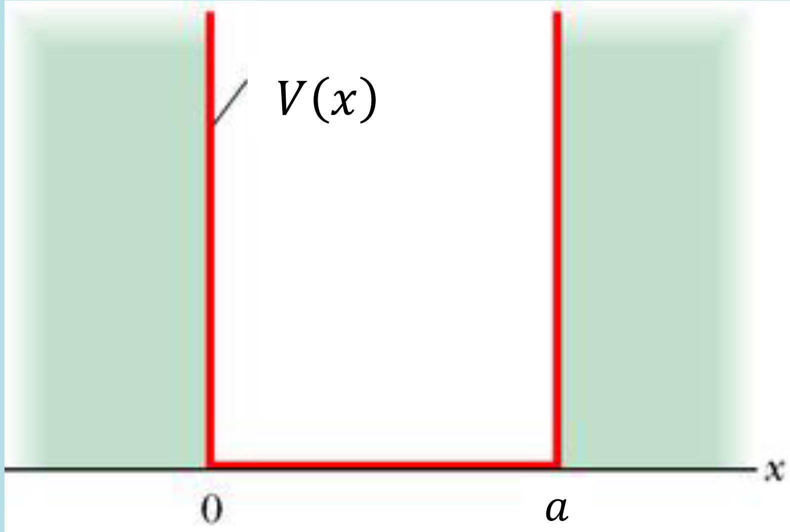
接著討論一個典型的束縛態。

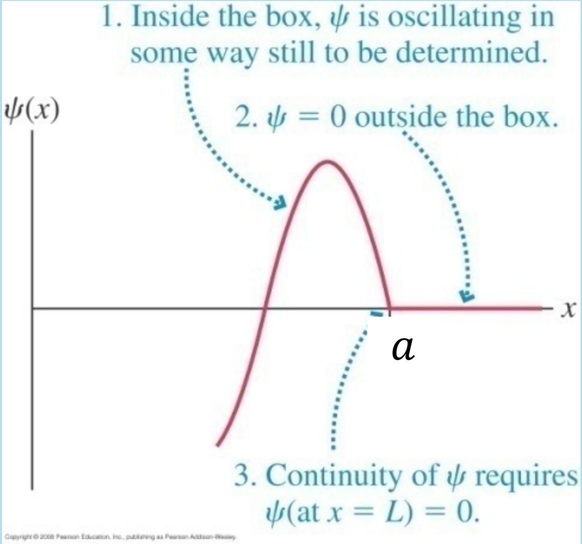
無限位能井，盒子中自由電子的定態。

$$V(x) = \infty \quad x < 0$$
$$= 0 \quad 0 < x < a$$
$$= \infty \quad a < x$$









邊界外的位能是無限大，波函數必須為零。否則位能期望值會是無限大！

邊界內波函數，必須在邊界上與邊界外波函數連續，

因此邊界內波函數在邊界上必須為零。

邊界條件，對任何時間： $\Psi(0,t) = \Psi(a,t) = 0$

$\psi_E(0) = 0$ $\psi_E(a) = 0$

金屬中的傳導電子所感受的位能就類似位能井。

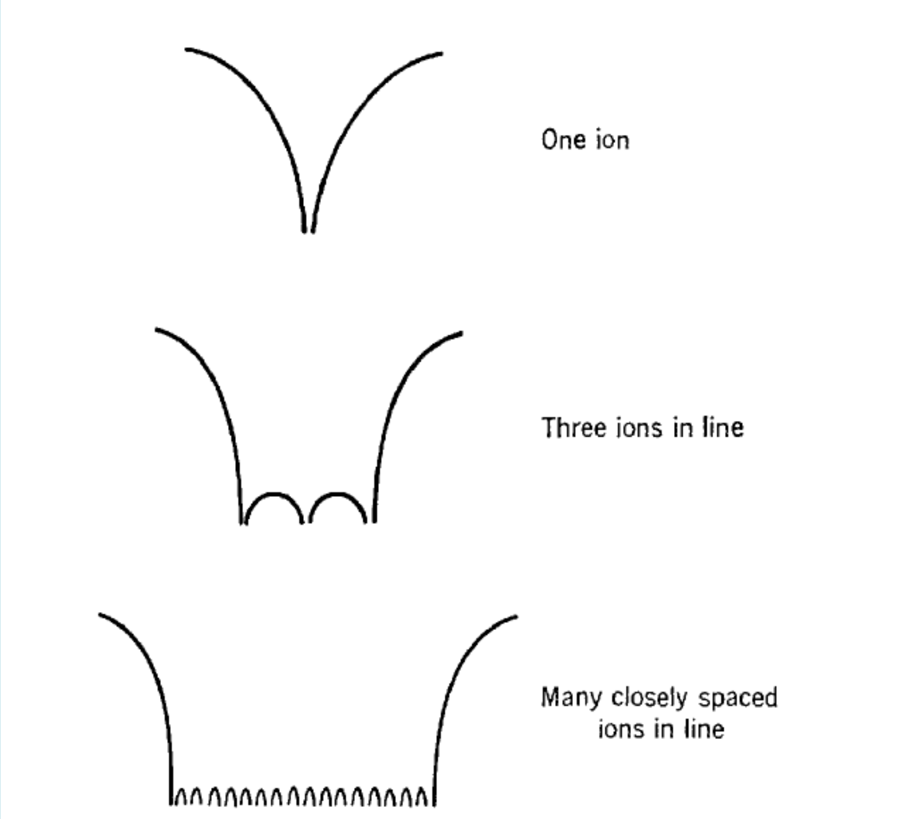
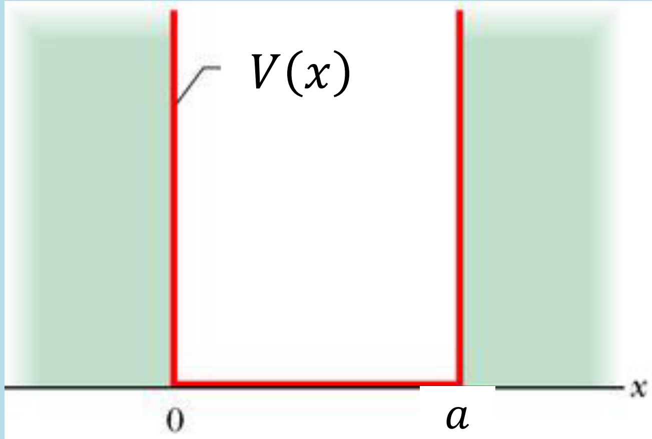


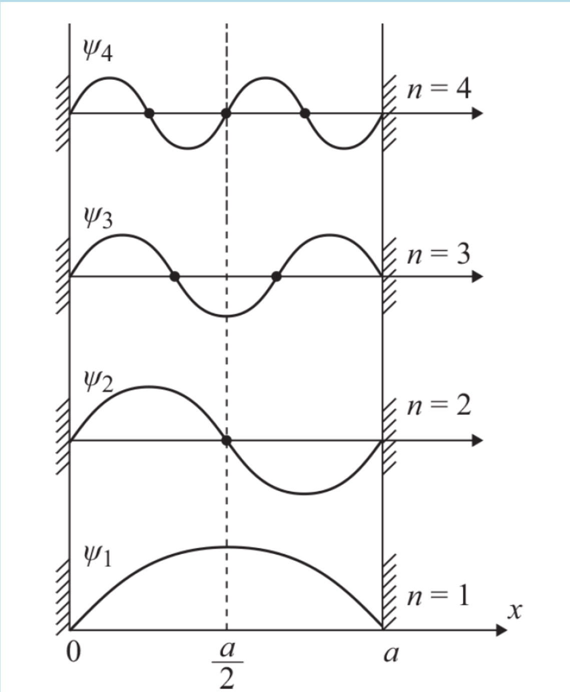
Figure 6-24 A qualitative indication of how an approximation to a square well potential results from superimposing the potentials acting on a conduction electron in a metal. The potentials are due to the closely spaced positive ions in the metal.

有邊界之自由電子



邊界條件：

$\psi_E(0)=0$　　$\psi_E(a)=0$



在邊界內，如同自由電子，因此可延用自由電子波。

$$\frac{d^2\psi_E}{dx^2}=-\frac{2mE}{\hbar^2}\psi_E \equiv -k^2\psi_E \qquad k\equiv\sqrt{\frac{2mE}{\hbar^2}}$$

$$\frac{d^2\psi_E}{dx^2}=-k^2\psi_E$$

$$\psi_E=Ae^{ikx}+Be^{-ikx}$$

但必須加上邊界條件：

$$\psi_E(0)=0 \longrightarrow A+B=0$$

$$\psi_E=Ae^{ikx}-Ae^{-ikx}=2iA\sin kx$$

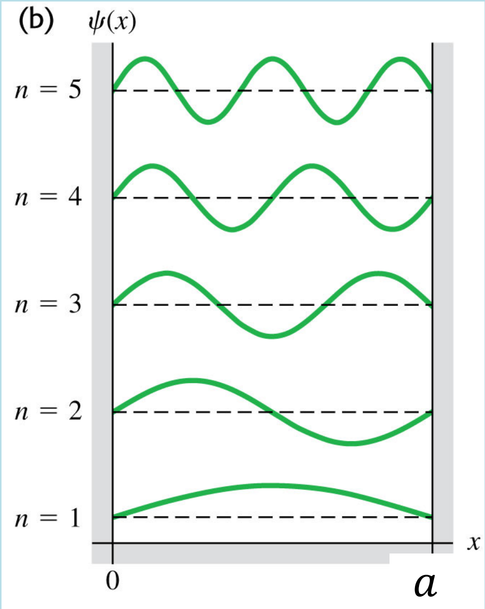
$$\psi_E=C\sin kx$$　重新定義常數：$C\equiv 2iA$

$$\psi_E(a)=0 \longrightarrow \psi_E(a)=C\sin ka=0$$

$$ka=n\pi$$　n是自然數。

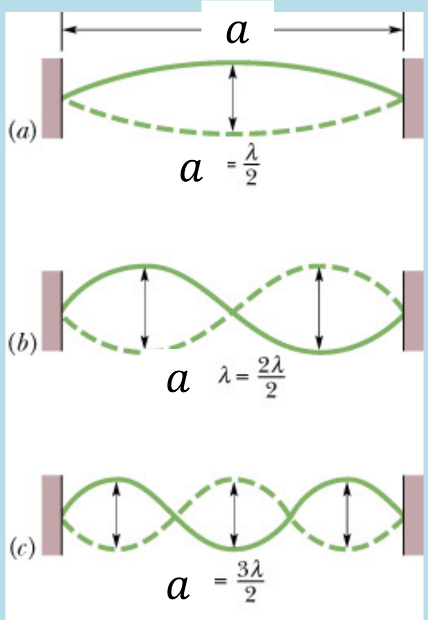
$$\psi_n=C\sin\left(\frac{n\pi}{a}x\right) \qquad k=\frac{n\pi}{a}$$

結果與弦波駐波的波函數的空間部分幾乎一模一樣！



$$k = \frac{n\pi}{a}$$

$$\frac{\lambda}{2} = \frac{a}{n}$$



解可以以量子數n編號，給它一個新的符號u_n：

$$\psi_n = u_n(x) = C\sin\left(\frac{n\pi}{a}x\right)$$

$$y = \left(y_m \cdot \sin\frac{n\pi}{a}x\right) \cdot \cos\omega t$$

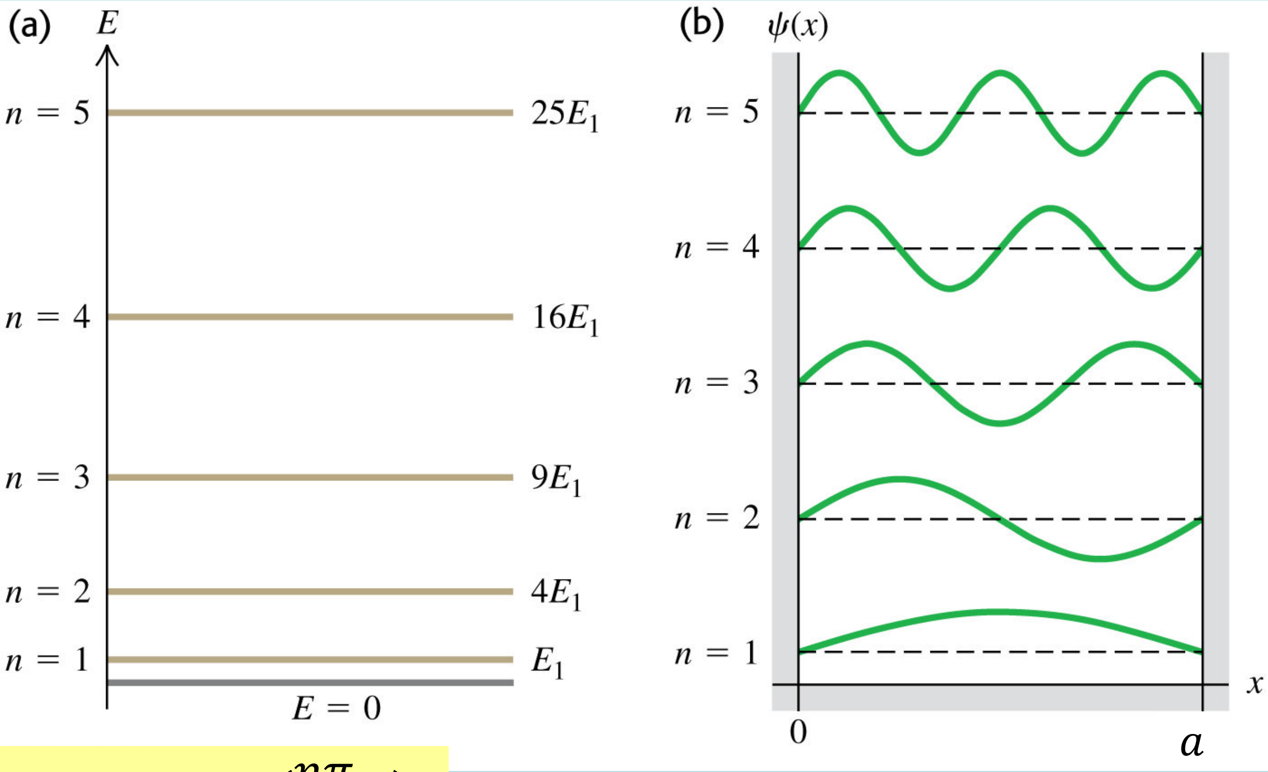
原則上常數C可以是任意複數。

但只有C的絕對值對物理有影響，常常就取C為實數。如此u_n就完全是實數函數，

但波函數Ψ_n還要乘上時間的部分。完整的解並不是實數！

$$\Psi_n(x,t) = C\sin\left(\frac{n\pi}{a}x\right) \cdot e^{-i\omega t}$$

有邊界之電子束縛態波函數的實數部如同駐波，但它必得有虛數部。



$$u_n = C\sin\left(\frac{n\pi}{a}x\right)$$

代回去與時間無關的薛丁格方程式：

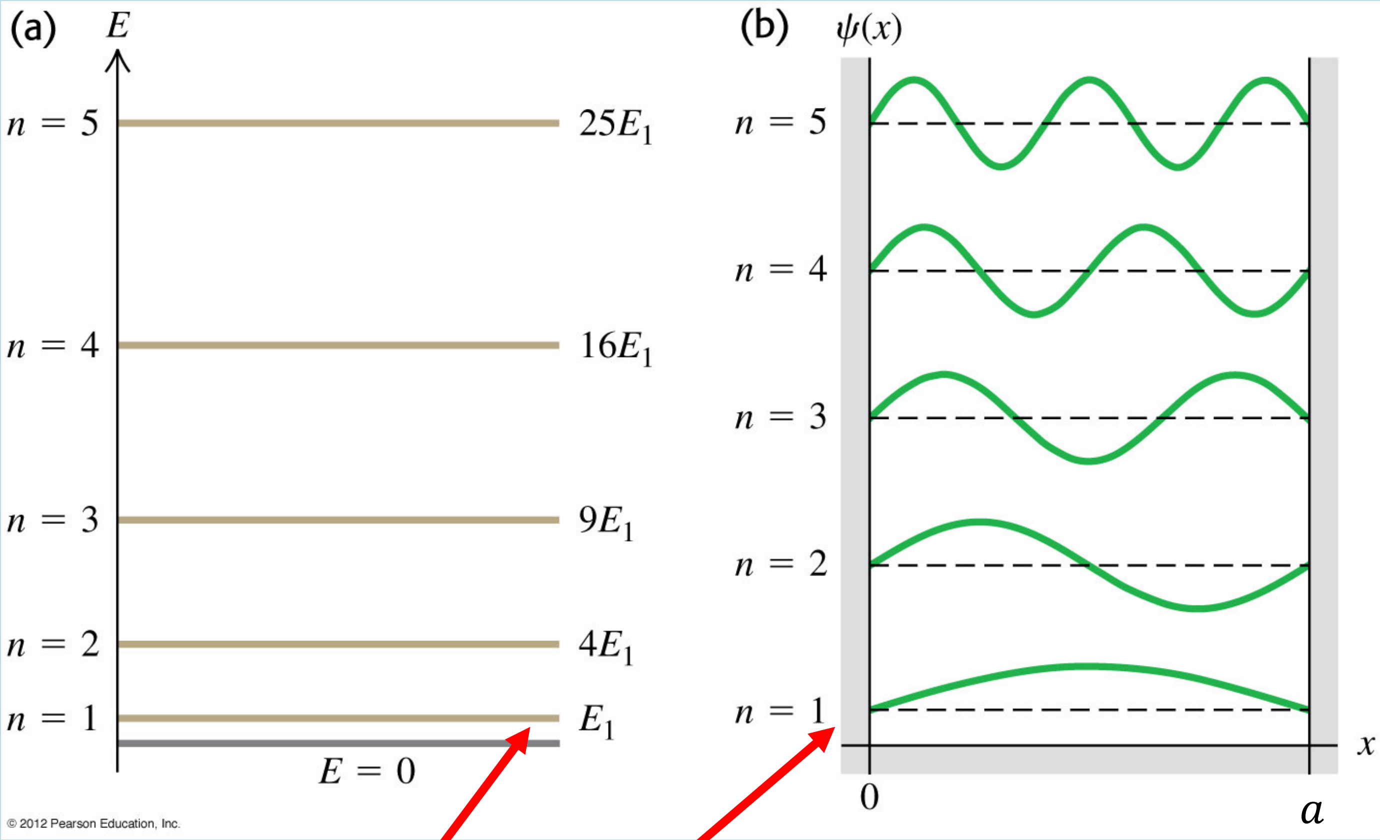
$$-\frac{\hbar^2}{2m}\frac{d^2\psi_E(x)}{dx^2} = E\psi_E(x) = \left(\frac{\hbar^2}{2m}\right)\frac{\pi^2}{a^2}n^2\psi_E(x)$$

能量E等於：

$$E_n = \left(\frac{\hbar^2}{2m}\right)\frac{\pi^2}{a^2}n^2 = \left(\frac{h^2}{8ma^2}\right)n^2$$

能量只有在這些值，與時無關薛丁格方程式才有滿足邊界條件的解！

這些定態，能量是量子化。將會證明無限位能井的任意解，能量測量值只會是E_n。



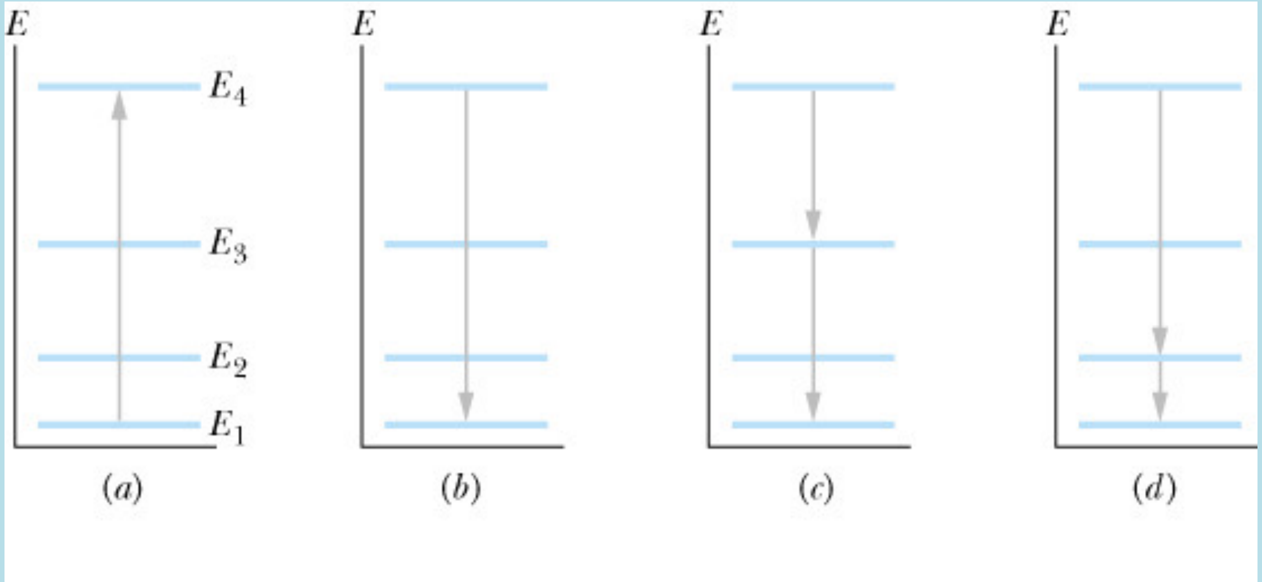
$$E_1 = \left(\frac{h^2}{8ma^2}\right)$$

有一能量最低的基態，能量不為零！

注意基態的動量不為零。

電子是靜不下來的！

這是測不準原理的結果。



電子可以在能階定態之間以放出與吸收光子的方式躍遷。

$$hf = \Delta E$$

到達基態後，電子是穩定的。

基態的存在是量子力學重要的特徵！

總機率必須等於 1

$$\int_0^a |\Psi_n(x,t)|^2 dx = \int_0^a |u_n(x)|^2 dx = 1$$

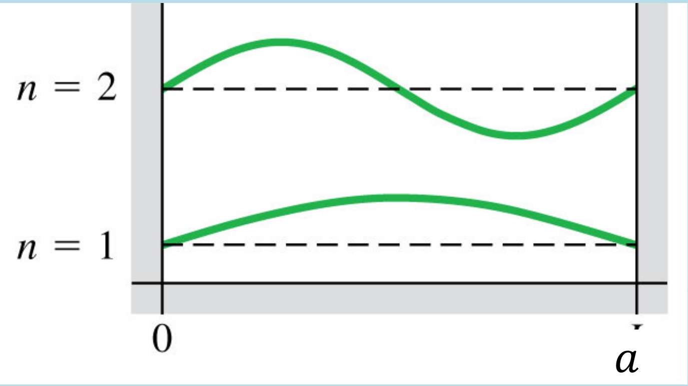
由歸一化條件可以解出係數 C

$$\int_0^a |C|^2 \left[\sin\left(\frac{n\pi}{a}x\right)\right]^2 dx = |C|^2 \int_0^a \left[\frac{1-\cos\left(2\frac{n\pi}{a}x\right)}{2}\right] dx = |C|^2 \frac{a}{2} = 1$$

$$|C| = \sqrt{\frac{2}{a}}$$

$$u_n = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right)$$

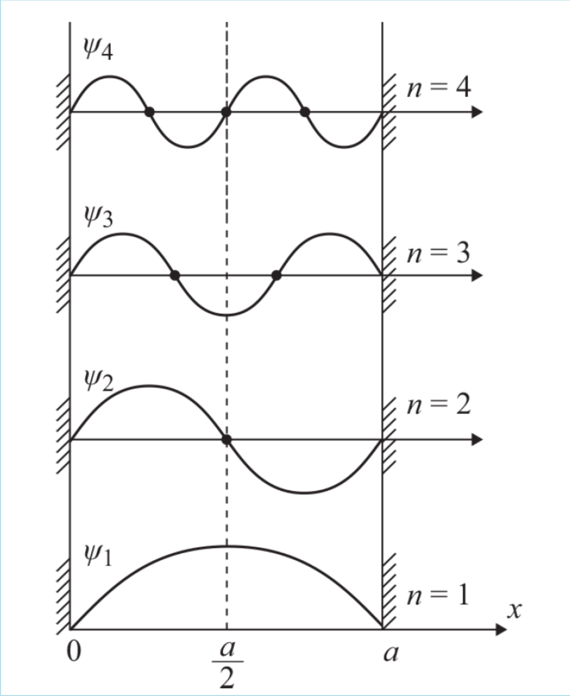
只有C的絕對值對物理有影響。所以常就直接取實數。



機率密度

$$P = |u_n(x)|^2 = \frac{2}{a}\left[\sin\left(\frac{n\pi}{a}x\right)\right]^2$$

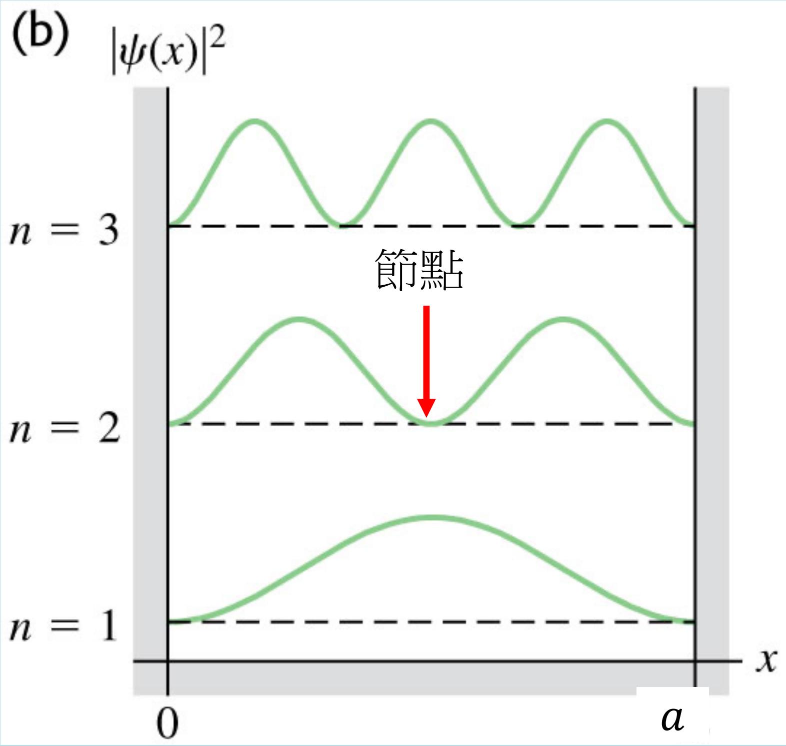
$$P\left(\frac{m}{n}a\right) = 0, m < n$$ 稱為節點。



在節點處，P一直為零，永遠不可能發現該電子！

此電子靜不下來，但在節點卻永遠找不到它！

注意：$n-1$即是節點數目！

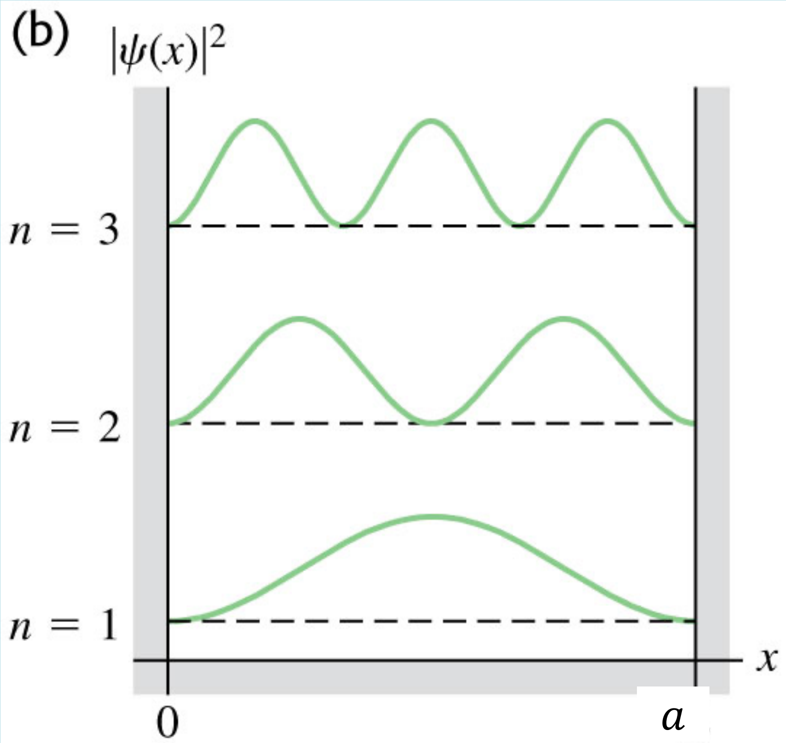


我們很容易就計算這些定態解的各個期望值：

因為對稱的關係：

$$\langle x \rangle = \frac{a}{2}$$

$\langle x^2 \rangle$ =? 習題！



$$\langle \hat{p} \rangle = \int_{-\infty}^{\infty} dx \cdot \Psi^*(x) \cdot \left(-i\hbar \frac{\partial}{\partial x}\right) \Psi(x)$$

$$= -i\hbar \int_0^a dx \cdot u_n(x) \left(\frac{d}{dx} u_n(x)\right) = \int_0^a dx \cdot \frac{d}{dx} u_n^2$$

$$= \frac{-i\hbar}{2} [u_n^2(a) - u_n^2(0)] = 0$$

$$\langle p \rangle = 0$$

$\langle p^2 \rangle = ?$

$$u_n = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right)$$

$$\langle \hat{p}^2 \rangle = \int_{-\infty}^{\infty} dx \cdot \Psi^*(x) \cdot \left(-i\hbar \frac{\partial}{\partial x}\right)^2 \Psi(x)$$

$$= -\hbar^2 \int_0^a dx \cdot u_n(x) \left(\frac{d^2}{dx^2} u_n(x)\right) = -\left(\hbar \frac{n\pi}{a}\right)^2 \frac{2}{a} \int_0^a dx \cdot \left[\sin\left(\frac{n\pi}{a}x\right)\right]^2$$

$$= \left(\hbar \frac{n\pi}{a}\right)^2 \frac{2}{a} \int_0^a dx \cdot \left[\frac{1 - \cos\left(2\frac{n\pi}{a}x\right)}{2}\right] = \left(\hbar \frac{n\pi}{a}\right)^2 \frac{2}{a} \frac{a}{2} = \left(\hbar \frac{n\pi}{a}\right)^2$$

我們得到動量測量的不準度：

$$\Delta p \equiv \sqrt{\langle \hat{p}^2 \rangle - \langle \hat{p} \rangle^2} = \frac{\hbar \pi n}{a}$$

$$E_n = \left(\frac{\hbar^2}{2m}\right) \frac{\pi^2}{a^2} n^2$$

而且得到動量平方的期望值就是能量$2mE_n$ ！

$$\langle p^2 \rangle = \left(\hbar \frac{n\pi}{a}\right)^2 = (\hbar k)^2 = 2mE_n$$

這應該表示：

$$E_n = \langle \hat{H} \rangle = \left\langle \frac{\hat{p}^2}{2m} \right\rangle$$

E_n就是$\hat{H}$的期望值！這進一步驗證了期望值計算的方法是正確的。

位能下薛丁格方程式的普遍解法：

首先，位能下薛丁格方程式會有一系列的定態解：

$\Psi_n(x,t) = u_n(x) \cdot e^{-i\frac{E_n}{\hbar}t}$ 定態解就是時間部分與空間可以分離的解！

將$t = 0$時的波函數，即起始條件，對定態解u_n展開如下：

$$\Psi(x,0) = \sum_{n=1}^{\infty} A_n u_n(x)$$

$$u_n = C\sin\left(\frac{n\pi}{a}x\right)$$

這就是傅立葉分析！

$t = 0$時此狀態可以視為定態的如上疊加，

而接下來定態隨時間的演化，就是在u_n上乘$e^{-i\frac{E_n}{\hbar}t}$，這滿足位能薛丁格方程式。

乘完之後依同樣方式疊加，整個波函數也就滿足薛丁格方程式。

$$\Psi(x,t) = \sum_{n=1}^{\infty} A_n u_n(x) e^{-i\frac{E_n}{\hbar}t}$$

我們已經在自由薛丁格方程式用了這樣的策略！當時的正弦波就是定態。

這個程序原則上適用於任何位能。

=

各個配料分離烹煮

+

+

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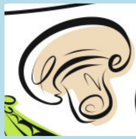

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⋮

Solving Wave Equation: $\frac{\partial^2 u}{\partial x^2} = \frac{1}{c^2}\frac{\partial^2 u}{\partial t^2}$,

8.2 THE METHOD OF SEPARATION OF VARIABLES

Since the additional conditions imposed on $u(x, t)$ in our string problem fall into two groups, (a) those involving x (boundary conditions) and (b) those involving t (initial conditions), it may be reasonable to seek solutions of the PDE in the form

$$u(x, t) = X(x)T(t),$$

where X is a function of x only and T is a function of t only. If $X(x)$ is chosen to satisfy the conditions

$$X(0) = 0, \qquad X(L) = 0,$$

then the function $u(x, t)$ will satisfy the same conditions. Then $T(t)$ may, perhaps, be chosen to satisfy the initial conditions.

We now reqûire that $u(x, t)$ satisfy the PDE. We have

$$\frac{\partial^2 u(x, t)}{\partial x^2} = \frac{d^2 X(x)}{dx^2} T(t), \qquad \frac{\partial^2 u(x, t)}{\partial t^2} = X(x)\frac{d^2 T(t)}{dt^2}.$$

Therefore

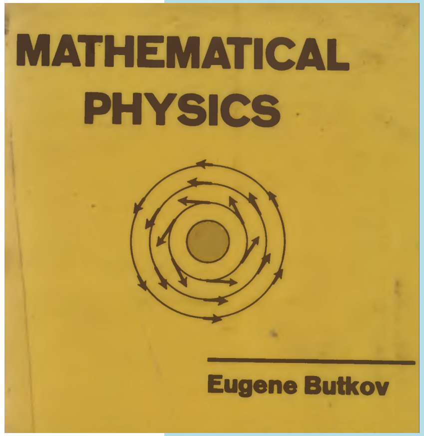
$$\frac{d^2 X}{dx^2} T = \frac{1}{c^2} X \frac{d^2 T}{dt^2}.$$

Dividing both sides by $X(x)T(t)$, we obtain

$$\frac{1}{X}\frac{d^2 X}{dx^2} = \frac{1}{c^2}\frac{1}{T}\frac{d^2 T}{dt^2}.$$

The left-hand side of this equation depends on x alone; the right-hand side depends on t alone. If this equality is to hold for all x and t, it is evident that either side must be a constant (same for both sides):

$$\frac{1}{X}\frac{d^2 X}{dx^2} = \lambda, \qquad \frac{1}{c^2}\frac{1}{T}\frac{d^2 T}{dt^2} = \lambda.$$



The constant λ is known as a *separation constant*. The equation for $X(x)$ can be written as

$$\frac{d^2X}{dx^2} = \lambda X$$

and will lead to exponential functions if $\lambda > 0$, to trigonometric functions if $\lambda < 0$, and to a linear function if $\lambda = 0$:

$$X(x) = \begin{cases} Ae^{x\sqrt{\lambda}} + Be^{-x\sqrt{\lambda}} & (\lambda > 0), \\ A' \cos(x\sqrt{-\lambda}) + B' \sin(x\sqrt{-\lambda}) & (\lambda < 0), \\ A''x + B'' & (\lambda = 0). \end{cases}$$

It is not difficult to verify that the boundary conditions $X(0) = 0$, $X(L) = 0$ can be satisfied *only* if $\lambda < 0$ and, moreover, *only* if A' is set equal to zero and the values of λ satisfy the condition

$$\sqrt{-\lambda} = n\pi/L \qquad (n = 1, 2, 3, \ldots).$$

Exercise. Show, in detail, that it is possible to satisfy either $X(0) = 0$ or $X(L) = 0$, but not both, if $\lambda \geq 0$. Also, prove the statement made for the case $\lambda < 0$.

These "allowed" values of the separation constant λ,

$$\lambda_n = -n^2\pi^2/L^2 \qquad (n = 1, 2, 3, \ldots),$$

are usually called the *eigenvalues*, or *characteristic values*, of the problem under consideration.* By this we mean the problem of finding functions satisfying the given DE *and* the given boundary conditions. In our case there is an infinity of such functions, called *eigenfunctions*, and they read

$$X_n(x) = B'_n \sin(n\pi x/L) \qquad (n = 1, 2, 3, \ldots),$$

where B'_n is an arbitrary (nonzero) constant which may, in general, be different for different eigenfunctions.

In our problem of the stretched string the function $T(t)$ which is multiplied by $X(x)$ must satisfy the DE with the same separation constant as $X(x)$. Therefore, to each eigenfunction $X_n(x)$ there corresponds a function $T_n(t)$ satisfying

$$\frac{1}{c^2}\frac{1}{T_n}\frac{d^2T_n}{dt^2} = \lambda_n = -\frac{n^2\pi^2}{L^2}.$$

This yields

$$T_n(t) = C_n \cos\frac{n\pi ct}{L} + D_n \sin\frac{n\pi ct}{L},$$

where C_n and D_n are arbitrary constants.

Summarizing our results we may say that the attempt to find the solution of our PDE with given boundary conditions and initial conditions in the form

$$u(x, t) = X(x)T(t)$$

leads us, so far, to an *infinite number* of such functions which may be written as

$$u_n(x, t) = \left(A_n \cos\frac{n\pi ct}{L} + B_n \sin\frac{n\pi ct}{L}\right) \sin\frac{n\pi x}{L},$$

where $A_n = B_n'C_n$ and $B_n = B_n'D_n$ are arbitrary constants. Each of these functions $u_n(x, t)$ satisfies the PDE and the boundary conditions. It remains for us to select from among these functions, adjusting the constants A_n and B_n, those functions that will also satisfy the desired initial conditions. Before we do this, however, note that each function $u_n(x, t)$ represents, on its own, *some* kind of possible motion of the stretched string (corresponding to some special initial conditions). These types of motion are known as the *characteristic modes* (or *normal modes*) of vibration of the string. Each one represents a harmonic motion (vibration) with the characteristic frequency (or "eigenfrequency")

$$\omega_n = n\pi c/L \qquad (n = 1, 2, 3, \ldots).$$

be true for a linear combination of a *finite* number of functions $u_n(x, t)$. It is not unreasonable to conjecture that the same properties will hold for an *infinite series* formed by the functions $u_n(x, t)$:

$$y(x, t) = \sum_{n=1}^{\infty} \left(A_n \cos \frac{n\pi ct}{L} + B_n \sin \frac{n\pi ct}{L} \right) \sin \frac{n\pi x}{L},$$

provided the series converges (or if not, provided it can be treated as a distribution, in conformity with the principles stated in Chapter 6).

It is needless to emphasize that the function $y(x, t)$ is a Fourier sine series in x (it is also a Fourier series in t, but this fact is of much less importance). Setting $t = 0$ and using the first initial condition, we obtain

$$u(x, 0) = u_0(x), \qquad u_0(x) = \sum_{n=1}^{\infty} A_n \sin \frac{n\pi x}{L}.$$

If the function $u_0(x)$ can be expanded into a Fourier sine series, the coefficients A_n can be determined. In physical problems $u_0(x)$ is invariably continuous, piecewise very smooth, and vanishes at $x = 0$ and $x = L$. Therefore, it can be represented as above.

Similarly, calculating $(\partial u/\partial t)(x, t)$ and using the second initial condition, we can obtain

$$\frac{\partial u}{\partial t}(x, 0) = v_0(x) \qquad v_0(x) = \sum_{n=1}^{\infty} B_n \frac{cn\pi}{L} \sin \frac{n\pi x}{L}.$$

In physical problems $v_0(x)$ is sometimes assumed to be discontinuous. However, it is invariably piecewise continuous and piecewise very smooth, and the coefficients B_n can be determined as well.

Consequently, we have constructed a solution to our problem in the form of a series

$$y(x, t) = \sum_{n=1}^{\infty} \left(A_n \cos \frac{n\pi ct}{L} + B_n \sin \frac{n\pi ct}{L} \right) \sin \frac{n\pi x}{L},$$

which satisfies the boundary conditions and initial conditions for all physically reasonable functions $u_0(x)$ and $v_0(x)$.